

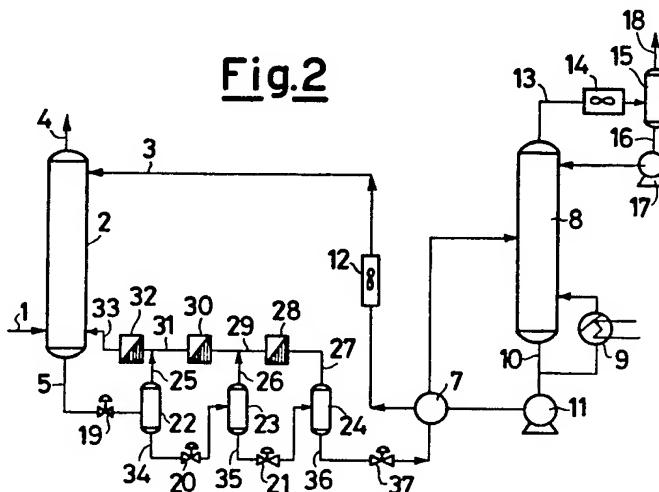
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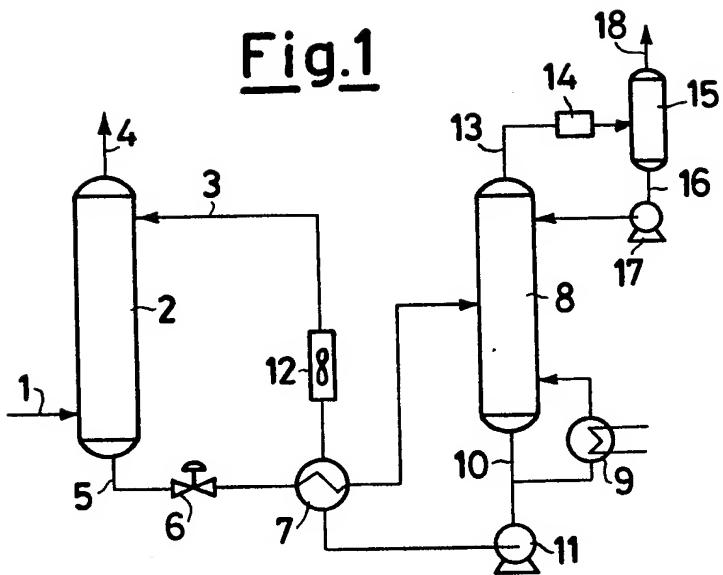
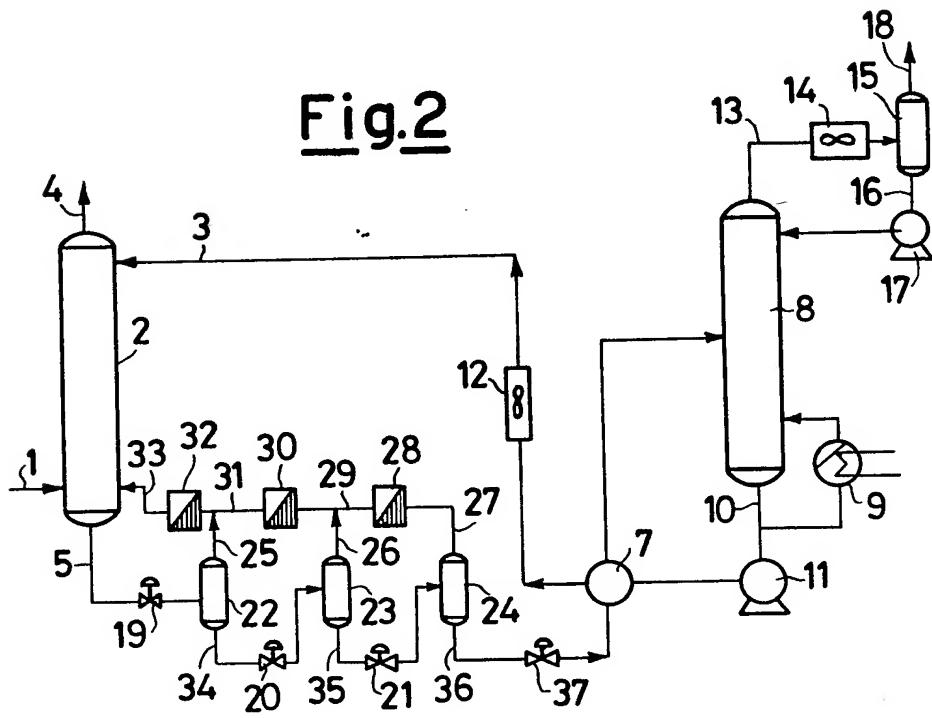
(54) Process for selectively
removing hydrogen sulphide from
gaseous mixtures containing also
carbon dioxide

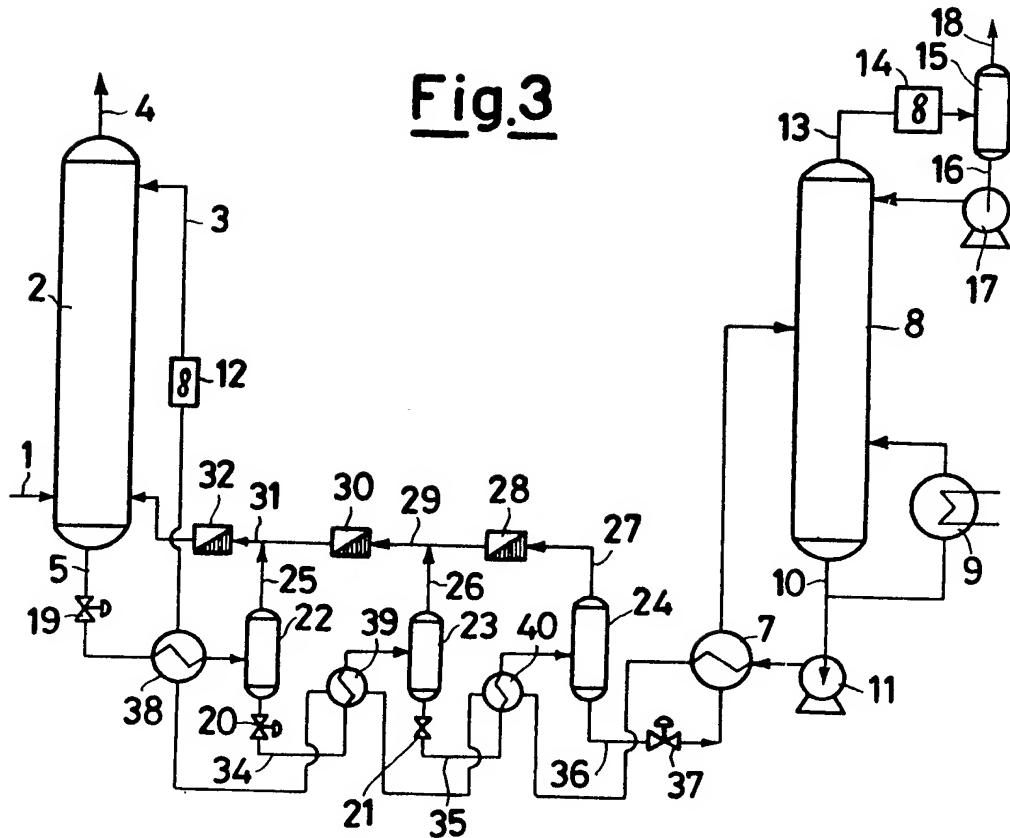
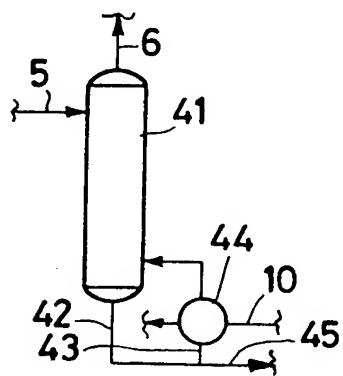
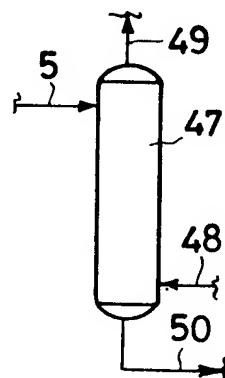
(57) A process is disclosed for
selectively removing hydrogen
sulphide from gaseous mixtures also
containing carbon dioxide, essentially
comprising an absorption in a column
by means of a mixture of a tertiary
amine and an organic solvent with a
water concentration not greater than
25% by weight, and a regeneration
in a column for the distillation of the
exhausted absorbent mixture,
characterized in that said exhausted
mixture before being regenerated in
the distillation column undergoes a
partial regeneration in one or more
steps, the separation being obtained
of a gas having a CO₂/H₂S ratio
greater than that of the exhausted
mixture leaving the absorption
column.



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Fig.1Fig.2

Fig.4Fig.5

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Fig.6

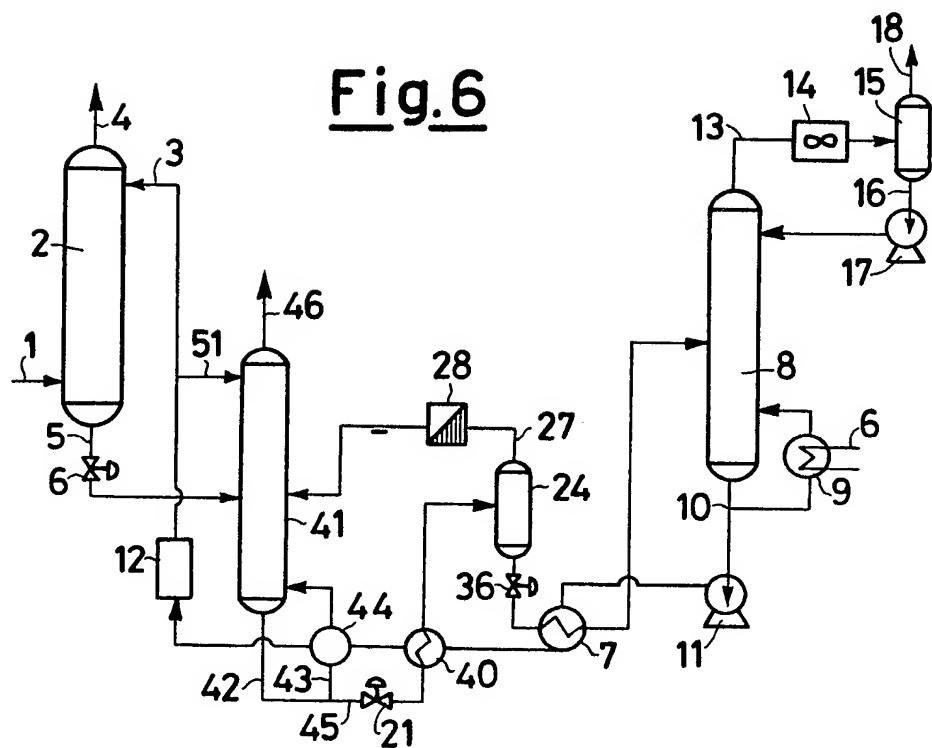
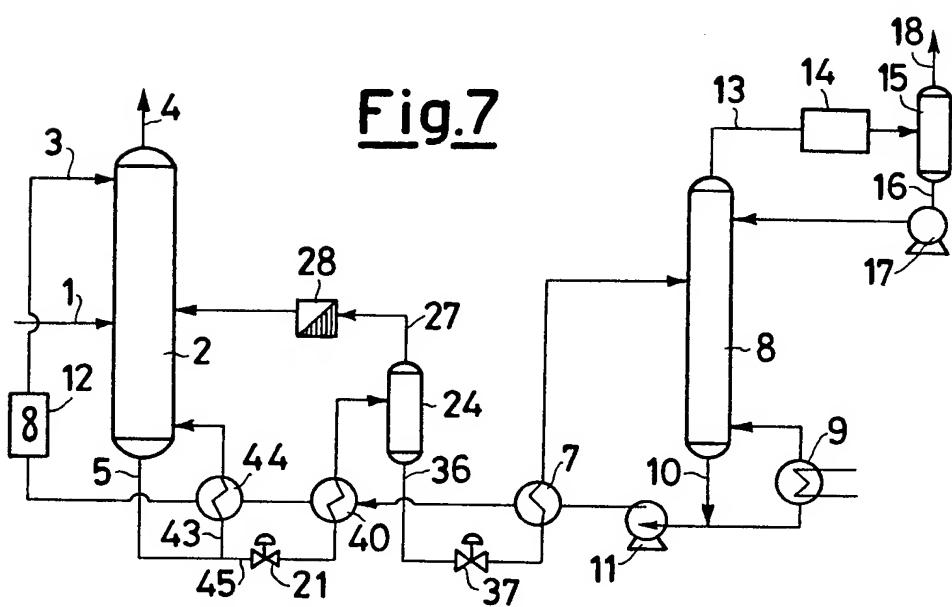


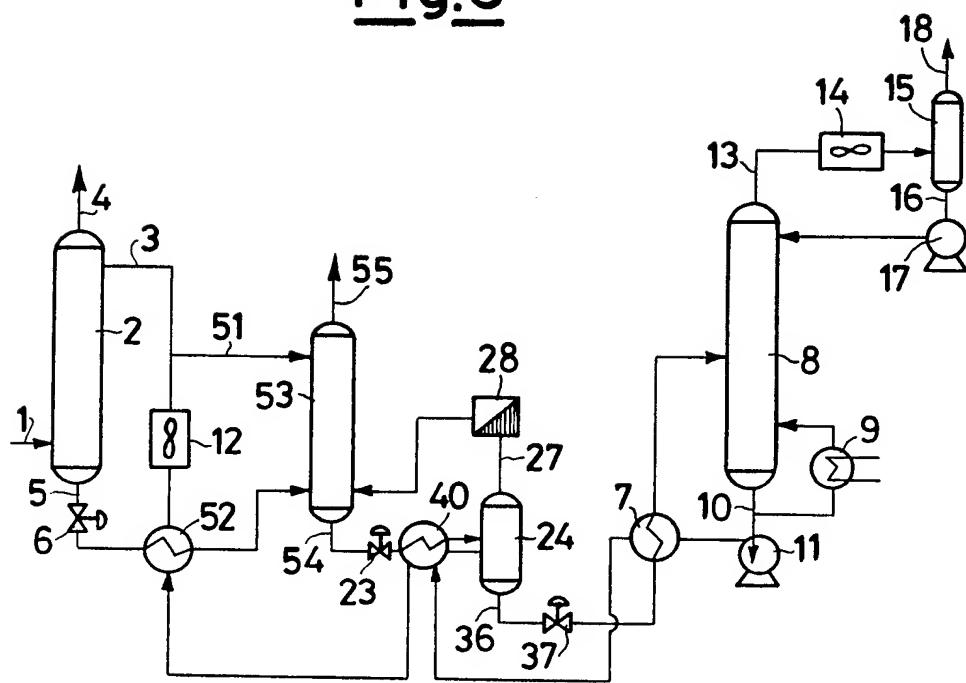
Fig.7



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Fig.8



SPECIFICATION

Process for selectively removing hydrogen sulphide from gaseous mixtures containing 5 also carbon dioxide

The present invention relates to a process for the selective separation of hydrogen sulphide from gaseous mixtures containing also carbon dioxide, by means of a mixture of a tertiary amine and an organic solvent in aqueous solution.

It is known from the U.K. Patent 2079307 granted on 10.5. 1984 in the same applicant's name the use as the absorption means a mixture of a tertiary amine and of an organic solvent with a water content not higher than 10% by weight.

We illustrate the process being the object 20 of said Patent Application by means of the scheme of attached Fig. 1.

By means of the pipe 1, the gas to be processed is delivered to the absorber 2, to which the absorbent solution is supplied via 25 the pipe 3.

From the top of the absorber 2 the processed gas is drawn via the pipe 4.

The exhausted absorbent solution is discharged from the absorber 2 by means of the 30 pipe 5, is expanded in the valve 6, heated in the heat exchanger 7, and sent to the regeneration column 8 equipped with the reboiler 9.

From the bottom of the column 8 the regenerated solution 10 is sent to the column 2 35 by the pump 11, after having been cooled first in 7 by the exhausted stream 5, and then in 12 by a fan.

From the head of the column 8 the acidic 40 gases 13 containing the H₂S absorbed by the solution outcome, and are cooled in 14 and separated in 15 into a liquid stream 16, which is recycled by the pump 17 to the regenerating column 8, and a gas 18 containing H₂S.

By the said process the obtainment is possible 45 of a treated gas substantially free from H₂S, and of a gaseous stream mainly consisting of H₂S and CO₂, enriched in H₂S relatively to the relative H₂S and CO₂ amounts in the raw gas.

Whilst for most applications the enrichment 50 in H₂S of the acidic gas stream is more than enough, some cases exist in which a higher selectivity may be desirable. Obtaining a higher selectivity is particularly advantageous

55 when the acidic gases must be fed to a Claus plant for sulphur production, to the purpose of reducing the gas volumes fed to the Claus plant. The selectivity is also important when CO₂ is to be used (as chemical product, or for alimentary use, or for the raws' assisted recovery), and has hence a value by its own, so that after the selective plant a conventional plant for CO₂ recovery is installed; in this case, minimizing the CO₂ amount lost together

60 with H₂S is obviously advantageous.

The increase in selectivity is usually obtained in the plants operating with aqueous tertiary amines, with a second selective treatment, i.e. by using the so-called "concentrator" plant. In such a plant, the stream of acidic gases is processed again, producing a still more concentrated H₂S stream. This of course requires considerable additional investment expenses and involves greater consumptions of related utilities.

70 One of the reasons why the concentrator plant is particularly burdensome is the fact that the acidic gas stream is produced at a pressure slightly higher than the atmospheric pressure, so that also the reabsorption of H₂S in the concentrator plant occurs at a slightly super-atmospheric pressure, and hence under particularly disadvantageous conditions. On the other hand, recompressing the whole acidic

75 gas stream would result too expensive.

80 We have found a process allowing the selectivity in H₂S removal from the gas mixture containing also CO₂ to be increased.

85 The process being the object of the present invention, comprising essentially an absorption in a column by means of a tertiary amine and of an organic solvent with a water content not greater than 25% by weight and a regeneration in a distillation column of the exhausted

90 absorbent mixture, is characterized in that said exhausted absorbent mixture is submitted, before being regenerated in the distillation column, to a partial regeneration in one or more steps, the separation being obtained of a gas having a CO₂/H₂S ratio greater than that of the exhausted mixture leaving the absorption column.

95 The gas as obtained from the partial regeneration can be recycled to the main absorption column, or to another absorption column.

100 The partial regeneration can be carried out by expansion or by heating or by stripping, or by means of one or more exhausting columns, or by means of a suitable combination of 105 these treatments, and can be repeated a suitable number of times. The regeneration steps may be equal to or different from each other.

110 The partial regeneration by expansion consists in expanding the exhausted solution to an intermediate pressure between the absorption pressure and the regeneration pressure, and separating the gases formed.

115 This process may be repeated more than once, greater selectivities being obtained with a greater number of intermediate expansions.

120 It has been found however that the selectivity increase decreases when passing from the second to the third expansion, so that in practice providing more than three intermediate expansions in series between the absorber and the regeneration column is not suitable.

125 The partial regeneration by heating consists in a heating of the exhausted mixture, e.g., by using the heat of the mixture regenerated in 130 the regeneration column, and in the separation

of used gases.

The heating occurs under the pressure of the absorption column, or at an intermediate pressure between the absorption pressure and 5 the regeneration pressure.

The partial regeneration by means of one or more exhausting columns, is carried out by operating under the same pressure as of the absorption column, or under a pressure intermediate between the absorption pressure and 10 the regeneration pressure.

Another possible embodiment of the invention consists in allowing a slight heating between the expansion and the separation, thus 15 a further selectivity increase being obtained.

This heating is of the order of 5–25°C, according to the selectivity increase desired, and to the number of expansion stages used. If more than one stages are used, it is generally 20 convenient a higher heating degree before the first stage, the subsequent heatings being lower and lower.

The partial regeneration by stripping consists in stripping the exhausted mixture with a 25 H₂S-free gaseous mixture, operating under the same pressure as of the absorption pressure, or under an intermediate pressure between the absorption and the regeneration pressures.

As examples of gas streams which can be 30 used to that purpose, we can mention fuel gas or the nitrogen available from the air fractionation unit in the plants for synthesis gas production by partial oxidation.

These gas streams may be used as well in 35 the strippers and in the exhausting column, in addition to the heat action, in the nearby of the reboiler, or immediately above, or some trays under the same reboiler, in an additional adiabatic stripping column.

40 The partial regeneration may comprise also an intermediate heating inside the exhausting column and/or the stripping column.

All these systems, besides improving the 45 selectivity of H₂S relatively to CO₂, have also another advantage: the heavy hydrocarbons are noticeably reduced, by being co-absorbed with H₂S in the exhausted solution, if they are present in the raw gas. It is known that these heavy hydrocarbons, when present in the supply 50 to the Claus plant, can impair the quality of sulphur, in particular the colour thereof.

According to another embodiment of the 55 present invention, the gases obtained from the partial regeneration in the expansion stages, are compressed to the pressure of the highest partial regeneration stage and H₂S is reabsorbed with a portion of the regenerated mixture. A CO₂ stream substantially free from H₂S becomes hence available for possible uses.

60 The tertiary amines which can be used either individually or as mixtures with each other are dimethylethanamine, ethyldiethanamine, propyldiethanamine, dipropylethanamine, isopropyldiethanamine, diisopropy-

65 lethanamine, methyldiisopropanolamine,

ethyldiisopropanolamine, propyldiisopropanolamine, isopropyldiisopropanolamine, N-methylmorpholine.

The solvents which may be used either individually or as mixtures with each other as components of the solution are sulpholane, N-methylpyrrolidone, N-methyl-3-morpholone, dialkylethermonoethyleneglycols, dialkyletherpolyethyleneglycols (wherein each one of the alkyl groups contains from 1 to 4 carbon atoms), N,N-dimethylformamide, N-formylmorpholine, N,N-dimethylimidazolin-2-one and N-methylimidazole.

The invention shall be now better disclosed 80 with the aid of the flow charts of Figs 2, 3, 4, 5, 6, 7 and 8 hereto attached, representing embodiments preferred, but which are not to be considered as limitative of the invention itself.

85 The flow chart of fig. 2 represents a process provided with three partial regeneration steps, constituted by an expansion in valve, under a pressure intermediate between the absorber pressure and the regeneration column 90 pressure, and subsequent separation of developed gases, which are recycled to the absorber.

By means of the pipe 1 the gas to be treated is sent to the absorption column 2, to 95 which the absorption solution too is fed via the pipe 3. Within the column 2, which can be equipped with trays, or with a packing of conventional type, the gas to be processed and the absorption solution flow in countercurrent to selectively remove H₂S.

From the top of the column 2 the treated 100 gas (hydrocarbons+CO₂) is drawn by the pipe 4.

The exhausted absorption solution is discharged 105 from the column 2 through the pipe 5 and is partly regenerated in three steps, by expansion in the valves 19, 20 and 21 and separation in the separators 22, 23 and 24.

From the top of the separators 22, 23 and 110 24 three gas streams 25, 26 and 27 come out, with CO₂/H₂S ratios greater than the streams 5, and decreasing relatively to each other.

The stream 27 is compressed in 28 to the 115 same pressure as of the stream 26, and is combined with the same; the formed mixture 29 is compressed in 30 to the pressure as of the stream 25, and is combined with it; the next mixture formed 31 is compressed in 32 to the pressure as of the absorber 2 and is recycled by 33 to the same absorber.

The liquid streams 34 and 35 leaving from 125 the separators 22 and 23 are respectively sent into the separators 23 and 24, whilst the liquid stream 36 leaving from the separator 24 is first expanded in the valve 37, then pre-heated in the heat exchanger 7, and finally fed to the distillation column 8 provided with the reboiler 9 to complete the regeneration.

130 From the bottom of the column 8 the re-

generated solution 10 is sent to the column 2 by means of the pump 11, after having been first cooled in 7 with the partly regenerated stream 36 and then air-cooled by means of 5 the fan 12.

From the head of the column 8 there come out the acidic gases 13 containing the H₂S absorbed by the solution, which gases are cooled by means of the fan 14, and are sent 10 into the separator 15 from whose bottom a liquid stream 16 is drawn and recycled to the regeneration column by means of the pump 17. From the head of the separator 15 a H₂S-containing gas 18 comes out.

15 The flow chart of fig. 3 represents a process having three partial regeneration steps constituted each by a heating, by an expansion in valve and by a separation of the developed gases, which are recycled to the absorber.

20 Relatively to the flow chart of fig. 1, the additional exchangers 38, 39 and 40 are provided, which respectively heat the streams 5, 34 and 35 after having been expanded in 25 valve.

The heat is supplied by the regenerated solution 10 before being recycled to the absorber 2.

In fig. 4 a partial regeneration step is 30 shown, which uses an exhausting column.

The exhausted solution 5 enters the exhausting column 41 from whose bottom a stream 42 is drawn, a portion 43 of which is heated in 44 by thermal exchange, e.g., with 35 the regenerated solution 10, whilst the remaining portion 45 is sent to a second partial regeneration stage or to the regeneration column.

From the head of the column 41 a gas 40 stream 46 enriched in CO₂ comes out.

In fig. 5 the partial regeneration step using a stripping column is used.

The exhausted solution 5 enters the stripping column 47 into the bottom of which a gas 45 stream is fed by means of the pipe 48. From the head of the stripper a gas 49 enriched in CO₂ comes out, whilst from the bottom a stream 50 is drawn and is sent to a second 50 partial regeneration step or to the regeneration column.

The flow chart of fig. 6 represents a process provided with two regeneration stages wherein the first stage is an exhausting column, and the second one is constituted by an 55 expansion, a heating and a separation.

The exhausted solution 5 coming out of the absorber 2 is fed, after having been expanded in 6, to the exhausting column 41, from whose bottom a solution 42 comes out, 60 which is partly (43) recycled to the same column, after having been heated in 44 by means of the regenerated solution 10, and partly (45) is expanded in the valve 21, heated in 40 and separated in 24. From the 65 bottom of the separator 24 a liquid stream 36

is drawn and is sent, as in preceding schemes, to the regeneration column 8; from the head of the separator a gas 27 leaves which is compressed in 28 to the pressure of 70 the exhausting column 41 and recycled to the same column.

H₂S in the column 41 is reabsorbed by a portion of the regenerated solution 10, i.e., the stream 51, so that from the head a 75 stream 46 containing CO₂ and substantially free from H₂S comes out.

The flow chart of fig. 7 represents a process simplified relatively to the preceding process, having two regeneration stages, wherein 80 the first stage is an exhausting column operating under the same pressure as of the absorption column, and the second is constituted by an expansion, a heating and a separation.

The exhausted solution 5 coming out of the 85 absorber 2 is partly (43) recycled to the absorber 2, after having been heated in 44 by means of the regenerated solution 10, partly (45) expanded in the valve 21, heated in 40 and separated in 24. From the bottom of the

90 separator 24 a liquid stream 36 is drawn and is sent to the regeneration column 8 similarly to the preceding schemes, whilst from the head a gas 27 comes out, which is compressed in 28 to the pressure of the column 2 95 and is then recycled to the same column.

The flow chart of fig. 8 represents a process with two absorption columns and with a partial regeneration stage constituted by an expansion, a heating and a separation.

100 The solution 5 leaving the absorber 2 after having been expanded in 6 and heated in 52 with the regenerated solution 10 is fed to a second absorber 53, from whose bottom comes out a solution 54, which is expanded in 23, heated in 40 and separated 24.

From the bottom of the separator 24 a liquid stream 36 is drawn which is sent, similarly to the preceding schemes, to the regeneration column 8; from the head of the separator 24 a gas 27 comes out, which is compressed in 28 to the pressure of the absorber 53, and recycled to the same absorber.

110 The H₂S in the absorber 53 is reabsorbed by the stream 51, which is a portion of the regenerated solution 10, so that from the head a stream 55 of CO₂ substantially free from H₂S comes out.

As Example is now supplied to the purpose of better illustrating the invention, which 115 example should not be considered as a limitation to the same invention. Said Example shall be followed by a Comparison Example.

Example 1

A natural gas, available under 56 kg/cm², with 4.5% by volume of H₂S and 64% by volume of CO₂ is treated with a dimethylethanolamine solution at 40% by weight, of N-methylpyrrolidone at 50% by weight and water (10%) by weight, according to the pro-

cess as schematically shown in fig. 8.

There are obtained a purified gas with less than 1 ppm of H₂S, a stream of acidic gases containing 71.93% by volume of H₂S, a stream of CO₂ with less than 1 ppm of H₂S under a pressure of 15 kg/cm³, representing 11.6% of the CO₂ contained in the raw gas.

(Comparison) Example 2

- 10 The same natural gas is treated according to the process as schematically shown in fig. 1 (known art), with the same type of solution, a purified gas being obtained with less than 1 ppm of H₂S, and a stream of acidic gases 15 being obtained, containing about 32.65% by volume of H₂S. It can be noticed hence that, besides yielding a stream of CO₂ substantially free from H₂S, the process claimed according to the present Patent Application yields a 20 stream of acidic gases containing 71.93% by volume of H₂S, with a decrease of the volume of gases fed to the Claus process of 2.2 times relatively to the known art.

Attention is drawn to the related application 25 filed by us on the same day as the present application.

CLAIMS

1. A process for selectively removing hydrogen sulphide from a gaseous mixture also 30 containing carbon dioxide, which comprises subjecting the gaseous mixture to absorption in a column by means of a mixture of a tertiary amine and of an organic solvent with a 35 water content not greater than 25% by weight, and subjecting the exhausted absorbing mixture to regeneration in a distillation column; wherein the tertiary amine is selected from one or more of dimethylethanolamine, 40 ethyldiethanolamine, propyldiethanolamine, di-propylethanolamine, isopropylidethanolamine, diisopropylethanolamine, methyldiisopropanolamine, ethyldiisopropanolamine, propyldiisopropanolamine, isopropyldiisopropanolamine 45 and N-methylmorpholine; wherein the organic solvent is selected from one or more of sulpholane, N-methylpyrrolidone, N-methyl-3-morpholone, dialkylethermonoethyleneglycols, dialkyletherpolyethyleneglycols, N,N-dimethylformamide, N-formylmorpholine, N,N-dimethylimidazolin-2-one and N-methylimidazole; and 50 wherein the exhausted absorbing mixture is submitted, before being regenerated in the distillation column, to a partial regeneration in one or more stages thereby to obtain the separation of a gas having a CO₂ : H₂S ratio 55 greater than the exhausted absorbing mixture from the absorption column.
2. A process according to claim 1, wherein 60 the gas obtained from the partial regeneration is recycled to the absorption column.
3. A process according to claim 1 or 2, wherein the partial regeneration is effected by expansion.
- 65 4. A process according to claim 1 or 2,

wherein the partial regeneration is effected by heating.

5. A process according to claim 1 or 2, wherein the partial regeneration is effected by 70 stripping.

6. A process according to claim 1 or 2, wherein the partial regeneration is effected by the use of one or more exhausting columns.

7. A process according to claim 1 or 2, 75 wherein the partial regeneration is effected by expansion and/or by heating and/or by stripping and/or by the use of one or more exhausting columns.

8. A process according to claim 7, wherein 80 the number of stages of partial regeneration is from 1 to 3.

9. A process according to claim 3, wherein the partial regeneration by expansion consists in expanding in a valve the exhausted mixture 85 to a pressure intermediate the absorption pressure and the regeneration pressure, and in separating the gas formed.

10. A process according to claim 4, wherein the partial regeneration by heating 90 consists in heating the exhausted mixture and in separating the resulting gas.

11. A process according to claim 10, wherein the heating is effected by using the heat of the regenerated mixture.

95 12. A process according to claim 10 or 11, wherein the heating is effected under the pressure of the absorption column, or under a pressure intermediate the absorption pressure and the regeneration pressure.

100 13. A process according to claim 12, wherein the exhausting column operates under the same pressure as the absorption column, or under a pressure intermediate the absorption pressure and the regeneration pressure.

105 14. A process according to claim 5, wherein the partial regeneration by stripping consists in stripping the exhausted mixture with a H₂S-free gas stream.

110 15. A process according to claim 14, wherein the stripping is effected under the same pressure as the absorption column or under a pressure intermediate the absorption pressure and the regeneration pressure.

115 16. A process according to claim 13, wherein stripping gas is fed to the exhausting column in the vicinity of a reboiler, or immediately above the reboiler, or to one or more plates under the reboiler.

120 17. A process according to any of claims 1 to 16, wherein the partial regeneration stages are the same as or different from each other.

125 18. A process according to claim 12 and/or claim 14, wherein the partial regeneration also comprises a heating step upstream of the exhausting column and/or of the stripping operation.

19. A process according to claim 3, wherein the gases obtained from the partial regeneration in the expansion stages are com-

pressed to the pressure of the highest partial regeneration stage, the H₂S contained therein being then reabsorbed with a portion of the regenerated mixture.

- 5 20. A process according to claim 1, substantially as hereinbefore described with reference to any of Figs. 2 to 8 of the drawings.

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